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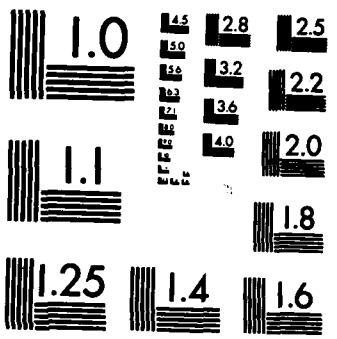

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REACTIONS OF METAL-METAL MULTIPLE BONDS. 14. SYNTHESIS AND CHARACTERIZATION OF TRIANGULO-W_3 AND Mo_2W-oxo CAPPED ALKOXIDE CLUSTERS. COMPROPORTIONATION OF M-M TRIPLE BONDS, $\sigma^2\pi^4$ AND d^0 METAL-oxo GROUPS: $M{\equiv}M + M{\equiv}O \longrightarrow M_3(\mu_3\text{-}O)$

by

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In hydrocarbon solvents $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and $WO(O\text{-}i\text{-}Pr)_4$ react to give $W_3O(O\text{-}i\text{-}Pr)_{10}$. Similarly $Mo_2(O\text{-}i\text{-}Pr)_6$ and $WO(O\text{-}i\text{-}Pr)_4$ yield the mixed metal cluster $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ but the reaction between $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and $MoO(O\text{-}i\text{-}Pr)_4$ proceeds further to give by oxo group transfer $WO(O\text{-}i\text{-}Pr)_4$ along with other products. Attempted comproportionations involving $Mo_2(O\text{-}i\text{-}Pr)_6$ and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ with either $M(O\text{-}i\text{-}Pr)_5$ (M = Nb and Ta) or $W(NPh)(O\text{-}i\text{-}Pr)_4$ failed to react. The new triangulo oxo capped alkoxides are isomorphous and

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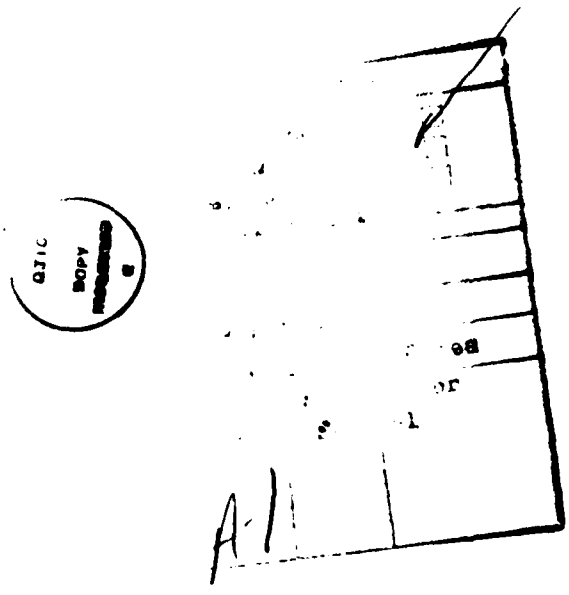
isostructural with the previously reported $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ compound. The electronic absorption spectra and electrochemical data are consistent with a common electronic structure and a gradation of properties for the replacement of Mo by W.



Reactions of Metal-Metal Multiple Bonds. 14. Synthesis and Characterization of Triangulo-W_3 and Mo_2W-oxo Capped Alkoxide Clusters. Comproportionation of M-M Triple Bonds, $\sigma^2\pi^4$ and d^0 Metal-oxo Groups: $M{\equiv}M + M{=}O \longrightarrow M_3(\mu_3\text{-}O)$.

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ABSTRACT

In hydrocarbon solvents $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and $WO(O\text{-}i\text{-}Pr)_4$ react to give $W_3O(O\text{-}i\text{-}Pr)_{10}$. Similarly $Mo_2(O\text{-}i\text{-}Pr)_6$ and $WO(O\text{-}i\text{-}Pr)_4$ yield the mixed metal cluster $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ but the reaction between $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and $MoO(O\text{-}i\text{-}Pr)_4$ proceeds further to give by oxo group transfer $WO(O\text{-}i\text{-}Pr)_4$ along with other products. Attempted comproportionations involving $Mo_2(O\text{-}i\text{-}Pr)_6$ and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ with either $M(O\text{-}i\text{-}Pr)_5$ (M = Nb and Ta) or $W(NPh)(O\text{-}i\text{-}Pr)_4$ failed to react. The new triangulo oxo capped alkoxides are isomorphous and isostructural with the previously reported $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ compound. The electronic absorption spectra and electrochemical data are consistent with a common electronic structure and a gradation of properties for the replacement of Mo by W.

INTRODUCTION

The early transition elements niobium, molybdenum and tungsten have recently been found to exhibit an extensive trinuclear chemistry with a variety of ligands.[1,2] Even the Mo(IV) aquo ion has been shown by a variety of spectroscopic techniques to contain the trinuclear unit $Mo_3O_4^{4+}$.[3,4,5] These complexes have triangulo M_3 units capped by either one or two μ_3-X groups (X may be O, S, CR, etc.). The metal atoms are coordinated to 6 or 7 ligand atoms and the M_3 units have 4-8 cluster electrons. Our interest in these compounds was heightened by the discovery of the simple comproportionation reaction shown in eq. 1.[6,7] This provided a high yield synthesis of a new subset of triangulo cluster compounds.

$$\underset{\sim}{1} \quad (RO)_3Mo{\equiv}Mo(OR)_3 + (RO)_4MoO \longrightarrow$$

$$Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6$$

[R = i-Pr and CH_2-t-Bu]

Reaction 1 has a parallel with the syntheses of dinuclear and trinuclear complexes employing metal-alkylidyne or -alkylidene fragments.[8] Reaction 1 also has a parallel with the reactions of alkynes with $Mo_2(OR)_6$ compounds which give $Mo_2(\mu\text{-}C_2R_2)$ compounds containing the pseudo tetrahedral M_2C_2 core.[9] One might well wonder whether or not one could extend comproportionation reactions of type 1 to include other metal atoms and other ligands, e.g. can one replace Mo by W, O by S, NR and OR by SR etc. We describe here our initial findings which were prompted by these considerations.

RESULTS AND DISCUSSION

Synthesis

$W_3O(O\text{-}i\text{-}Pr)_{10}$. Since $W_2(O\text{-}i\text{-}Pr)_6$ is not isolable in an unligated form,[10] the crystalline compound $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$[11] was used along with $WO(O\text{-}i\text{-}Pr)_4$[12] for the comproportionation reaction. Mixing the two compounds in hexane followed by heating gave a royal blue solution from which dark blue crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ were obtained.

$Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. The addition of $WO(O\text{-}i\text{-}Pr)_4$ to a hexane solution of $Mo_2(O\text{-}i\text{-}Pr)_6$ followed by heating results in an orange to green color change, and by crystallization the mixed metal triangulo compound $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ can be isolated as green crystals.

$MoW_2O(O\text{-}i\text{-}Pr)_{10}$. In an attempt to prepare the related MoW_2-containing compound, $MoO(O\text{-}i\text{-}Pr)_4$ and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were allowed to react in hexane. An immediate reaction occurred as evidenced by a color change to green. However, the reaction was more complicated than had been hoped. Attempts to crystallize the trinuclear compound failed. First fine white needles of the relatively insoluble compound $WO(O\text{-}i\text{-}Pr)_4$ were obtained. Then from crystallization of the filtrate blue-green crystals were obtained. The ^1H NMR spectrum of the latter indicated the presence of $W_3O(O\text{-}i\text{-}Pr)_{10}$ and other species, possibly the desired $MoW_2O(O\text{-}i\text{-}Pr)_{10}$.

Our interpretation of this is that the oxo group transfer reaction in eq. 2 is favored and by further reaction the $WO(O\text{-}i\text{-}Pr)_4$ with $W_2(O\text{-}i\text{-}Pr)_6$ and $MoW(O\text{-}i\text{-}Pr)_6$ yield $W_3O(O\text{-}i\text{-}Pr)_{10}$ and $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, respectively.

$$2 \quad MoO(O\text{-}i\text{-}Pr)_4 + W_2(O\text{-}i\text{-}Pr)_6 \longrightarrow$$

$$MoW(O\text{-}i\text{-}Pr)_6 + WO(O\text{-}i\text{-}Pr)_4$$

This suggestion finds support in the observations of Hoskins[13] who found that, while the homonuclear tert-butoxides failed to react ($M_2(O\text{-}t\text{-}Bu)_6$ + $(t\text{-}BuO)_4MO$, M = Mo and W), the addition of $(t\text{-}BuO)_4MoO$ to $W_2(O\text{-}t\text{-}Bu)_6$ in hydrocarbon solvents yielded an immediate color change from yellow-orange to green but with time the yellow-orange color returned and by crystallization only a mixture of homonuclear, Mo_2 and W_2, and the heteronuclear MoW hexatert-butoxides were obtained. The formation of $MoW(O\text{-}t\text{-}Bu)_6$ in this reaction can reliably be established by NMR spectroscopy and by mass spectrometry but it cannot be separated from the Mo_2- or W_2-containing compounds by crystallization. Thus we believe that in the present instance $MoO(O\text{-}i\text{-}Pr)_4$ and $W_2(O\text{-}i\text{-}Pr)_6$ react to give $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ but that this is unstable with respect to dissociation to $MoW(O\text{-}i\text{-}Pr)_6$ and $WO(O\text{-}i\text{-}Pr)_4$. The latter then react to give $W_3O(O\text{-}i\text{-}Pr)_{10}$, $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2(O\text{-}i\text{-}Pr)_6$.

Attempted Preparations of $MM'_2(O\text{-}i\text{-}Pr)_{11}$ Compounds where M = Nb or Ta and M' = Mo or W. Since it is possible for RO ligands to cap the triangle of metal atoms once, why not twice? In attempts to prepare compounds of formula $MM'_2(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$, hydrocarbon solutions of $M(O\text{-}i\text{-}Pr)_5$ (1 equiv) where M= Nb and Ta and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were mixed and heated. No evidence for a comproportionation reaction was found by NMR spectroscopy.

Attempted Preparations of $M_2W(NPh)(O\text{-}i\text{-}Pr)_{10}$ where M = Mo, W. Since RN ligands are isoelectonic with oxo groups and are known to be capable of bridging three metal atoms,[14] $W(NPh)(O\text{-}i\text{-}Pr)_4$ and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were mixed in hydrocarbon solvents. No reaction was observed in either case.

Solid State and Molecular Structures

$W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. Crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ were found to be isomorphous with $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ which was previously examined. The mixed metal complex is undoubtedly disordered with respect to the disposition of molybdenum and tungsten atoms and consequently was not studied in detail. In the space group $P\bar{1}$, there are two independent $W_3O(O\text{-}i\text{-}Pr)_{10}$ molecules in the unit cell, differing only slightly with respect to the conformations of the isopropyl groups. Atomic positional parameters are given in Table I. An ORTEP view of the central $M_3O(O)_{10}$ skeleton is shown in Figure 1. The atom number system employed is the same as that used previously for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ molecule where the two independent molecules were related by primed and unprimed numbers.

A comparison of the pertinent bond distances for the two pairs of independent molecules for M = Mo and W is given in Table II and a

similar comparison of bond angles is given in Table III. The trinuclear molybdenum and tungsten compounds are shown to be remarkably similar in many structural aspects. The W-W bond distances appear to be slightly longer than the Mo-Mo distances, though this is not really statistically significant (2.540(6) Å vs 2.534(5), respectively). This is to be contrasted to the situation found for the triangulo cluster ions $(M_3(\mu_3\text{-}O)_2(O_2CR)_6(H_2O)_3^{2+}$.[15] There, the W-W bond distances were observed to be significantly shorter than the Mo-Mo distances (2.746(2) Å vs. 2.759(4), respectively). It can also be seen that for the present complexes, the W-ligand distances are consistently slightly longer than the Mo-ligand distances by 0.01-0.02 Å, though this is at the limit of statistical creditabilty. For the $M_3(\mu_3\text{-}O)_2(O_2CR)_6(H_2O)_3^{2+}$ species, no such consistent differences in M-ligand bond lengths were found.[15]

The results for metal-metal bond distances are in sharp contrast to those found for comlexes containing triple or quadruple metal-metal bonds.[16] There the W-W distance is typically ca. 0.10 Å longer than the Mo-Mo distance. This has been attributed to extensive core-core repulsion interactions between the two tungsten atoms which are separated by only ca. 2.1 Å. For the triangulo clusters, the data suggests that the W-W core-core repulsions might still be noticeable at 2.54 Å (the present species), but not at 2.75 Å (the $M_3(\mu_3\text{-}O)_2(O_2CR)_6(H_2O)_3^{2+}$ species.[15] More extensive comparisons are obviously needed to establish these trends, and detailed calculations will probably be necessary to determine the relative importance of core-core repulsions, orbital overlaps and steric interactions.

Electrochemical and UV-Visible Characterizations

Previously, the electrochemical and spectroscopic properties of $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ have been correlated with electronic structure predicted by Fenske-Hall molecular orbital calculations.[17] The latter predicted the HOMO to be of e symmetry being primarily M-M σ-bonding in nature, and the LUMO was also of e symmetry but having a mixture of M-M π bonding and metal ligand π-antibonding character. The HOMO-LUMO gap was calculated to be rather small ca. 1.5 eV.

A comparison of the electrochemical data is given in Table IV. All three complexes exhibited a quasi-reversible reduction couple at large negative potentials. Even with internal resistance compensation, the $\Delta E_{1/2}(=E_{p,a}-E_{p,c})$ value (110-175 mV) was much greater than that expected for a reversible charge-transfer process (60 mV). Approximately equimolar concentrations of ferrocene were added to each sample, and the reversible behavior of its oxidation couple under the experimental conditions implies that the present couples are inherently irreversible. Since the anodic and cathodic current peak heights are quite similar and the electrochemically generated $Mo_3O(O\text{-}i\text{-}Pr)_{10}^{1-}$ species is stable for hours, the presumed origin of the irreversibility is slow charge-transfer kinetics.

Each complex also exhibits an irreversible oxidation wave at low positive potentials. No corresponding back wave was observed even at scan rates of 1 V/sec. Two or more product waves at negative potentials were observed to grow in upon cycling through the oxidative wave. The oxidized trimers are thereby implied to rapidly decompose, but the exact nature of these rearranged products has not been ascertained. The Mo_3 complex also exhibits a second reduction wave at ca. -2.4 V which

appears to be irreversible. No such corresponding wave was observed for the other two complexes.

The data for the three complexes show rather interesting trends. In comparing the Mo_3 and W_3 complexes, it is seen that both the oxidation and reduction processes occur at significantly more negative potentials for the W_3 complex. This is consistent with the generally observed phenomenon that, for medium to high oxidation states, third row transition metals are easier to oxidize and harder to reduce than their second row analogs. This then confirms that both the HOMO and LUMO are predominantly metal centered.

The couples for the Mo_2W species occur at intermediate potentials though not at values that would be predicted on pure statistical grounds. The reduction couple occurs at only a slightly more negative value than that for the Mo_3 complex. The implication is that the reduction is more heavily centered on the Mo centers than on W. The value for the Mo_2W oxidative couple is observed to be much closer to that for W_3 than for Mo_3, which implies that the oxidation process is predominantly W centered. This behavior is consistent with the general behaviorial differences between Mo and W noted above. Presumably, the Mo-W bonds are polarized in the fashion $Mo^{\delta-}$-$W^{\delta+}$, though we cannot quantitatively demonstrate this.

A comparison of the UV-visible absorption spectra is given in Figure 2 and data are given in Table V. Qualitatively, the spectra are quite similar consisting of two or more weak bands in the visible region and one or more very intense transitions in the UV region. The weak bands in the visible region were previously assigned for $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ as arising from transitions between metal centered orbitals,[17] with the lowest energy band corresponding to the allowed HOMO → LUMO

transition. The low intensity of these bands results from the predominant d orbital character of these orbitals. That the lowest energy transition for the W_3 complex occurs at higher energy and has greater intensity than for the analogous Mo_3 complex suggests greater metal-metal overlap and possibly stronger bonding interactions in the W_3 complex which would not be unexpected.

The assignment of the intense, high energy absorption bands is more speculative. It was previously suggested that these could be either M-M $\sigma \rightarrow \sigma^*$ transitions or alkoxide-oxygen lone pair to metal charge transfer transitions. The comparison of the Mo_3 and W_3 complexes shows a shift of these transitions to higher energy by 0.7 eV, with the Mo_2W complex exhibiting a transition at intermediate energy. Since the W_3 complex is found to be 0.7 V harder to reduce electrochemically than the Mo_3 complex, this is exactly the type of behavior expected for an $O \rightarrow M$ LMCT transition. This assignment therefore appears most likely. This places the alkoxide-oxygen lone pairs approximately 2 eV lower in energy than the metal centered HOMO which is in good agreement with the MO calculations.[17]

CONCLUDING REMARKS

Comproportion reactions analogous to those previously employed for the synthesis of $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ have allowed the successful syntheses of tritungsten and tungsten dimolybdenum oxo capped alkoxide clusters. The new compounds are structurally and spectroscopically similar to the Mo_3^{-} containing compounds. A number of factors may limit an extension of this approach tc trinuclear cluster syntheses, two of which are seen in this work. (1) Oxo atom transfer reactions may be thermodynamically favored and the oxo capped trinuclear cluster may be merely an intermediate enroute to products of oxo group transfer. This in some ways parallels reactions between alkynes and $(RO)_3W{\equiv}W(OR)_3$ compounds which may lead to $W_2(\mu\text{-}C_2R_2)$ containing compounds[18] or metathesis products $(RO)_3W{\equiv}CR'$.[19] (2) Either for electronic or steric reasons a comproportionation may not occur. This is seen here in the failure of niobium and tantalum penta-isopropoxides to react with the $M_2(OR)_6$ compounds. However, a more obvious extension of the comproportionation reaction would involve $ReO(OR)_4$ compounds to give 7e electron clusters, analogous to the $Mo_3O(OR)_{10}^{-}$ anion which may be prepared electrochemically. Also of interest to us is the substitution of S for O and SR for OR. These considerations form the basis for continuing studies in our laboratories.

EXPERIMENTAL SECTION

General Procedures and Instrumentation

Standard experimental techniques for the preparation and manipulation of air- and moisture-sensitive materials were employed. The compounds $Mo_2(O\text{-}i\text{-}Pr)_6$[20] and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$[21] were prepared by literature procedures.

Electronic absorption spectra were obtained with a Hitachi 330 recording spectrophotometer. Samples were run versus a solvent blank using matched 1 cm or 1 mm quartz cells. The cyclic voltammograms were obtained using a PAR 173 potentiostat, a PAR 175 programmer and a Houston 2000 XY recorder. A single-compartment cell was used with a platinum bead or gauze working electrode, a platinum wire auxiliary electrode and a 0.01 F $AgNO_3(CH_3CN)$/Ag wire pseudo-reference electrode. A 0.2 M solution of tetra-n-butylammonium hexafluorophosphate (TBAH) was employed as a supporting electrolyte. Scan rates were 200 mV/sec. Internal resistance (IR) compensation was employed. Equimolar amounts of ferrocene were added as an internal calibrant ($E_{1/2}$ = +0.08 V). The peak splitting for this couple with IR compensation was consistent with a reversible couple (60-65 mV).

Preparations

The preparations of $MO(O\text{-}i\text{-}Pr)_4$ compounds, where M = Mo[7] and W[12], have been reported previously, but the present procedure provides the simplest and quickest syntheses.

$WO(O\text{-}i\text{-}Pr)_4$. LiO-i-Pr (1.6 g, 24 mmol) was added to a solution of $WOCl_4$ (2.0 g, 5.8 mmol) in ether (40 mL) at 0°C, with stirring. The color of the solution lightened immediately from red-orange to pale-

yellow and gradually became white with a copious white precipitate. The solution was allowed to stir overnight (10 h) at room temperature. The solvent was then removed in vacuo and from the resulting solids $WO(O\text{-}i\text{-}Pr)_4$ (2.5 g, 95% yield) was isolated by sublimation at 70°C, 10^{-4} torr.

$MoO(O\text{-}i\text{-}Pr)_4$. $MoOCl_4$ (1.0 g, 4 mmol) was suspended in hexane (10 mL). Isopropanol (1.2 mL, 16 mmol) and Et_3N (2.2 mL, 16 mmol) were mixed with hexane (10 mL) and this solution was added dropwise to the suspension of $MoOCl_4$ in hexane. The solution became yellow with a copious white precipitate, though some darker materials stuck to the side of the flask. The solution was stirred overnight (10 h), then filtered. The solids were washed with hexane and the filtrate was collected and concentrated in vacuo to give a yellow oil which was distilled (55°C, 10^{-4} torr) yielding $MoO(O\text{-}i\text{-}Pr)_4$ (0.4 g, 30% yield based on Mo).

$W_3O(O\text{-}i\text{-}Pr)_{10}$. $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (0.43 g) and $WO(O\text{-}i\text{-}Pr)_4$ (0.23 g) were combined and dissolved in hexane (10 mL). The solution was refluxed for 2 h. The color changed from a dull-green to an intense royal-blue. The solvent was removed in vacuo and the solids dissolved in CH_2Cl_2 and recrystallized. Dark blue crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ (0.50 g, 76% yield) were obtained. Anal. calcd. for $W_3O(O\text{-}i\text{-}Pr)_{10}$: C, 31.11; H, 6.09; N, 0.00. Found: C, 31.03; H, 6.20; N, ε0.03%.

^1H NMR data recorded in CD_2Cl_2, +16°C, 220 MHz: δ (OC<u>H</u>) = 5.57(3H), 5.12(3H), 4.55(3H), 3.98(1H) septets; δ (OCH<u>Me</u>$_2$) = 1.59(18H), 1.32(18H), 1.09(6H), 1.01(18H), doublets, J_{HH} = 7 Hz.

$Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. $WO(O\text{-}i\text{-}Pr)_4$ (0.29 g) and $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.42 g) were combined and dissolved in hexane (10 mL). The solution was refluxed for 2 h during which time the color changed from yellow to a deep forest-green. The solvent was removed in vacuo and the solids

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recrystallized from CH_2Cl_2 yielding dark green crystals of $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ (0.55 g, 77% yield). Anal. Calcd. for $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$: C, 36.67; H, 7.18; N, 0.00. Found: C, 36.66; H, 7.08; N, <0.03%.

In benzene-d_6 as solvent at +21°C, the ^1H NMR spectrum was consistent with a non-fluxional molecule having a mirror plane of symmetry. This generates seven types of O-i-Pr ligands in the integral ration 1:1:1:1:2:2:2; four of O-i-Pr ligands are contained in the molecular plane of symmetry, six are not. We anticipate seven methyne resonances and observe δ (OC<u>H</u>) = 5.79(1H), 5.04(2H), 5.44(2H), 5.28(1H), 4.74(2H), 4.71(1H) and 4.08(1H) (septets). Ten methyl resonances of equal intensity are expected since the six O-i-Pr ligands not contained in the mirror plane of the molecule (2:2:2) contain diastereotopic methyl groups: δ (OCH<u>Me</u>$_2$) = 1.68, 1.64, 1.63, 1.62, 1.56, 1.53, 1.24 (overlapping pair), 1.18 and 1.13, doublets, J_{HH} = 7 Hz.

<u>Attempted Preparation of</u> $MoW_2O(O\text{-}i\text{-}Pr)_{10}$. $MoO(O\text{-}i\text{-}Pr)_4$ (0.10 g) and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (0.25 g) were mixed and dissolved in hexane (10 mL). The solution was warmed to reflux for 2 h during which time the solution became dark green. Upon removing solvent <u>in vacuo</u>, fine white needles crystallized from the solution. These were identified as $WO(O\text{-}i\text{-}Pr)_4$. The filtrate was dried <u>in vacuo</u> yielding a dark green solid. The ^1H NMR spectrum in benzene-d_6 showed many overlapping septets and doublets, too many for a $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ compound. Careful recrystallization of the dark green solids from CH_2Cl_2 solutions yielded a small quantity of dark blue crystals which were collected by filtration and identified by ^1H NMR spectroscopy as mostly $W_3O(O\text{-}i\text{-}Pr)_{10}$, but probably contaminated by $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ and other products.

Attempted Comproportionation Reactions Involving $W(NPh)(O\text{-}i\text{-}Pr)_4$. $W(NPh)(O\text{-}i\text{-}Pr)_4$ was prepared in a manner analogous to that described by Schrock and coworkers[22] for the synthesis of $W(NPh)(O\text{-}t\text{-}Bu)_4$. Stoichiometric amounts of the reagents $W(NPh)(O\text{-}i\text{-}Pr)_4$ and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (ca. 200-300 mg) were combined and dissolved in hexane. The solution was stirred for 3 days and/or heated to reflux for periods as long as 2 days. No apparent reaction occurred and this was confirmed by ^1H NMR spectroscopy of the solids obtained from stripping the solution to dryness.

Attempted Comproportionation Reactions Involving $M(O\text{-}i\text{-}Pr)_5$ (M = Nb, Ta) and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_2(HNMe_2)_2$. Stoichiometric amounts of the reagents $M(O\text{-}i\text{-}Pr)_5$ (M = Nb, Ta) and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (ca. 200-300 mg) were dissolved together in 10-20 mL of hexane. The solutions were allowed to stir at room temperature for as long as four days or heated at reflux for as long as two days. No apparent reaction occurred and this was confirmed by ^1H NMR spectroscopy of the solids obtained from stripping the solution to dryness.

Crystallographic Studies

General operating procedures and listings of programs have been given previously.[7] Crystal data are summarized in Table VI.

$W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. Preliminary examination of the samples indicated they were isomorphous with $Mo_3O(O\text{-}i\text{-}Pr)_{10}$. The mixed metal complex is undoubtedly disordered with respect to the location of the metal atoms and so no data were taken other than for the cell parameters: a = 21.324(13) Å, b = 21.874(14) Å, c = 10.235(5) Å, α = 98.79(3)°, β = 92.77(3(°, γ = 117.85(2)° , at -159°C.

Data were collected in the usual manner for the $W_3O(O\text{-}i\text{-}Pr)_{10}$ sample and the starting coordinates for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ sample were used. Because of the number of atoms involved in the refinement, no attempt was made to include hydrogen contributions.

A final difference Fourier synthesis was featureless, with several peaks of 0.9 to 1.3 e A^{-3} located in the vicinity of the six tungsten atoms. Scans indicated no absorption correction was necessary.

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Supplementary Materials. Anisotropic thermal parameters, complete listings of bond distances and angles, figures showing the atom number scheme and observed and calculated structure amplitudes for $W_3O(O\text{-}i\text{-}Pr)_{10}$. Ordering information is given on any current masthead page.

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Table 1: Fractional Coordinates and Isotropic Thermal Parameters for $W_3O(O\text{-}i\text{-}Pr)_{10}$ Molecule

Atom	10^4x	10^4y	10^4z	B_{iso}
W(1)	2300.3(3)	6929.0(3)	6229(1)	13
W(2)	3646.5(3)	7749.1(3)	6593(1)	14
W(3)	2789.1(3)	8261.5(3)	6602(1)	13
O(4)	2918(5)	7686(5)	7927(8)	12
O(5)	2911(5)	7618(5)	4895(8)	14
O(6)	3895(5)	8775(5)	6750(9)	20
O(7)	3095(5)	6663(5)	6102(10)	18
O(8)	1747(4)	7491(5)	6270(9)	16
O(9)	2634(5)	8775(5)	5312(9)	18
O(10)	1725(5)	6229(5)	4616(10)	21
O(11)	4332(5)	7849(5)	5313(10)	22
O(12)	4260(5)	7824(5)	8085(10)	18
O(13)	2727(6)	8851(5)	8114(9)	23
O(14)	1805(5)	6324(5)	7413(10)	24
C(15)	2910(9)	7579(8)	3443(16)	26
C(16)	2184(9)	7410(9)	2775(16)	29
C(17)	3514(9)	8289(10)	3201(17)	33
C(18)	4555(8)	9442(9)	6688(21)	38
C(19)	4337(11)	9979(10)	6387(26)	57
C(20)	5051(11)	9662(11)	7951(20)	46
C(21)	3156(8)	6050(7)	5570(18)	26
C(22)	3247(11)	6033(10)	4114(18)	41
C(23)	3773(9)	6057(8)	6430(21)	37
C(24)	1040(7)	7429(8)	6170(16)	22
C(25)	702(9)	7176(10)	4720(17)	32
C(26)	608(9)	6938(10)	7062(17)	32
C(27)	2577(10)	9414(10)	5487(17)	35
C(28)	1900(11)	9327(10)	5925(18)	36
C(29)	2634(13)	9617(12)	4075(20)	49
C(30)	1048(8)	5578(8)	4468(15)	23
C(31)	739(10)	5389(10)	3001(19)	45
C(32)	1164(9)	4988(8)	4888(20)	33
C(33)	4999(11)	7883(16)	5379(22)	66
C(34)	5527(14)	8323(29)	6169(29)	149
C(35)	5213(16)	7967(27)	3928(28)	132
C(36)	4217(8)	7824(10)	9458(17)	31
C(37)	4482(10)	7328(13)	9880(21)	50
C(38)	4649(11)	8580(12)	10306(20)	49
C(39)	2807(10)	8894(9)	9515(17)	32
C(40)	3142(13)	9681(10)	10205(22)	55
C(41)	2085(11)	8460(12)	9895(20)	51
C(42)	1915(8)	6382(8)	8835(15)	23
C(43)	1183(9)	5965(10)	9282(17)	33
C(44)	2405(11)	6072(12)	9145(20)	46
W(1)"	7205.8(3)	6931.7(3)	504(1)	13
W(2)"	8130.7(3)	8172.4(3)	1706(1)	10
W(3)"	8389.6(3)	7146.9(3)	167 (1)	10

O(4)"	7586(5)	7287(5)	2545(9)	15
O(5)"	8252(5)	7549(5)	9945(8)	15
O(6)"	9034(5)	8202(5)	2514(9)	14
O(7)"	7141(5)	7844(5)	688(9)	17
O(8)"	7597(5)	6231(4)	569(9)	14
O(9)"	9138(5)	7019(5)	838(9)	19
O(10)"	6865(5)	6633(5)	-1413(10)	20
O(11)"	8626(5)	8983(5)	844(9)	17
O(12)"	8064(5)	8715(5)	3309(9)	16
O(13)"	8508(5)	6776(5)	3204(9)	16
O(14)"	6281(5)	6352(6)	983(10)	27
C(15)"	8562(8)	7635(7)	-1295(13)	13
C(16)"	8186(8)	7894(7)	-2179(13)	23
C(17)"	9387(8)	8135(10)	-977(18)	35
C(18)"	9700(7)	8711(7)	3368(15)	16
C(19)"	9785(8)	8438(8)	4580(15)	22
C(20)"	10328(8)	8865(9)	2532(17)	28
C(21)"	6617(8)	8067(9)	379(16)	26
C(22)"	6820(10)	8431(9)	-849(17)	31
C(23)"	6623(9)	8591(8)	1585(17)	27
C(24)"	7490(9)	5533(8)	7(18)	29
C(25)"	7841(10)	5592(9)	8713(16)	33
C(26)"	6710(9)	4994(9)	-177(21)	41
C(27)"	9665(7)	6890(8)	1422(14)	16
C(28)"	9362(10)	6115(9)	1469(18)	34
C(29)"	10310(8)	7126(11)	672(19)	40
C(30)"	6173(9)	6120(10)	-2088(17)	36
C(31)"	6287(10)	5790(12)	6565(19)	48
C(32)"	5732(12)	6483(14)	7647(26)	71
C(33)"	8732(8)	9688(7)	1172(15)	18
C(34)"	9357(9)	10117(8)	2298(15)	26
C(35)"	8878(10)	9992(9)	-96(17)	32
C(36)"	8015(8)	8570(7)	4620(14)	17
C(37)"	7233(8)	8262(9)	4910(15)	26
C(38)"	8519(8)	9231(7)	5606(14)	19
C(39)"	8083(8)	6572(8)	4240(15)	24
C(40)"	8575(10)	6626(9)	5437(16)	30
C(41)"	7487(9)	5787(9)	3722(17)	35
C(42)"	5947(11)	6376(12)	2161(22)	73
C(43)"	5286(22)	6361(27)	1774(50)	171
C(44)"	5772(23)	5773(32)	2666(42)	207

Table II. Comparison of Bond Distances (A) in $M_3O(O\text{-}i\text{-}Pr)_{10}$ Molecules, M = Mo and W.

Bond	Molecule I		Molecule II	
	Mo	W	Mo	W
M(1)-M(2)	2.538(2)	2.5388(11)	2.534(2)	2.5433(11)
M(1)-M(3)	2.535(2)	2.5422(11)	2.528(2)	2.5363(10)
M(2)-M(3)	2.529(2)	2.5488(9)	2.528(2)	2.5381(10)
avg. [M-M]	2.537	2.543	2.530	2.539
M(1)-O(4)	2.064(8)	2.086(9)	2.055(7)	2.095(9)
M(2)-O(4)	2.064(8)	2.092(8)	2.058(8)	2.080(9)
M(3)-O(4)	2.068(8)	2.075(9)	2.059(8)	2.093(9)
avg. [M-(μ_3-O)]	2.065	2.084	2.057	2.089
M(1)-O(5)	2.173(8)	2.191(9)	2.155(7)	2.159(9)
M(2)-O(5)	2.172(8)	2.174(9)	2.157(7)	2.194(9)
M(3)-O(5)	2.165(7)	2.179(9)	2.139(7)	2.159(9)
avg. [M-(μ_3-OR)]	2.170	2.181	2.150	2.171
M(1)-O(7)	2.015(8)	2.034(9)	2.023(8)	2.040(9)
M(1)-O(8)	2.036(7)	2.058(9)	2.054(7)	2.063(9)
M(2)-O(6)	2.024(8)	2.021(10)	2.024(7)	2.025(9)
M(2)-O(7)	2.043(8)	2.052(9)	2.041(8)	2.046(9)
M(3)-O(6)	2.053(9)	2.067(10)	2.047(7)	2.059(9)
M(3)-O(8)	2.009(8)	2.030(8)	2.014(7)	2.021(9)
avg. [M-(μ-OR)]	2.043	2.044	2.034	2.042
M(1)-O(14)	1.891(8)	1.909(10)	1.905(8)	1.917(10)
M(2)-O(12)	1.910(8)	1.898(10)	1.912(7)	1.929(9)
M(3)-O(13)	1.893(8)	1.912(10)	1.912(8)	1.929(8)
avg. [M-OR]	1.898	1.906	1.910	1.925
M(1)-O(10)	1.952(7)	1.961(10)	1.959(8)	1.961(10)
M(2)-O(11)	1.953(8)	1.973(9)	1.945(8)	1.960(9)
M(3)-O(9)	1.950(8)	1.967(90	1.950(8)	1.960(9)
avg. [M-OR]	1.943	1.967	1.951	1.960

Table III. Bond Angles for the $M_3O(O\text{-}i\text{-}Pr)_{10}$ Molecules

Bond	Angle I		Angle II	
	Mo	W	Mo	W
M(2)-M(1)-M(3)	60.1(1)	60.215(27)	59.9(1)	59.957(28)
M(2)-M(1)-O(4)	52.1(2)	52.70(23)	52.0(2)	52.19(24
M(2)-M(1)-O(5)	54.2(2)	54.13(23)	54.1(2)	54.88(23)
M(2)-M(1)-O(7)	51.8(20)	51.92(27)	51.7(2)	51.60(26)
M(2)-M(1)-O(8)	110.8(2)	111.28(24)	110.7(2)	110.75(24)
M(2)-M(1)-O(10)	127.7(2)	126.8(3)	126.8(3)	125.9(3)
M(2)-M(1)-O(14)	123.9(2)	123.7(3)	127.9(3)	126.9(3)
M(3)-M(1)-O(4)	52.2(2)	52.14(24)	52.2(2)	52.70(25)
M(3)-M(1)-O(5)	54.1(2)	54.22(23)	53.7(2)	54.04(23)
M(3)-M(1)-O(7)	111.6(2)	111.89(27)	111.6(2)	111.56(26)
M(3)-M(1)-O(8)	50.7(2)	50.07(24)	50.9(2)	50.88(24)
M(3)-M(1)-O(10)	127.6(2)	127.0(3)	127.7(2)	127.3(3)
M(3)-M(1)-O(14)	126.8(2)	126.5(3)	125.6(3)	125.0(3)
O(4)-M(1)-O(5)	92.3(3)	92.6(3)	91.9(3)	93.1(3)
O(4)-M(1)-O(7)	87.3(3)	88.2(4)	83.6(3)	83.7(4)
O(4)-M(1)-O(8)	83.9(3)	83.7(3)	85.5(3)	86.1(4)
O(4)-M(1)-O(10)	179.7(3)	179.1(4)	178.8(3)	178.1(4)
O(4)-M(1)-O(14)	87.1(3)	86.6(4)	88.8(3)	87.4(4)
O(5)-M(1)-O(7)	81.1(3)	80.9(4)	85.1(3)	85.0(4)
O(5)-M(1)-O(8)	83.3(3)	83.7(3)	81.4(3)	80.9(4)
O(5)-M(1)-O(10)	87.4(3)	86.6(4)	87.2(3)	85.7(4)
O(5)-M(1)-O(14)	177.7(3)	177.5(4)	177.8(3)	177.8(4)
O(7)-M(1)-O(8)	161.7(3)	162.2(4)	162.4(3)	162.1(4)
O(7)-M(1)-O(10)	92.6(3)	92.0(4)	95.5(3)	94.7(4)
O(7)-M(1)-O(14)	96.7(3)	96.7(4)	97.1(3)	97.2(4)
O(8)-M(1)-O(10)	96.1(3)	95.9(4)	95.3(3)	95.2(4)
O(8)-M(1)-O(14)	98.8(3)	98.5(4)	96.5(3)	96.9(4)
O(10)-M(1)-O(14)	93.3(3)	94.3(4)	92.0(3)	93.8(4)
M(1)-M(2)-M(3)	59.9(1)	59.96(3)	59.9(1)	59.88(3)
M(1)-M(2)-O(4)	52.1(2)	52.48(24)	51.9(2)	52.75(25)
M(1)-M(2)-O(5)	54.3(2)	54.75(24)	54.0(2)	53.62(24)
M(1)-M(2)-O(6)	111.8(2)	112.08(27)	111.9(2)	112.05(25)
M(1)-M(2)-O(7)	50.8(2)	51.26(25)	51.1(2)	51.39(26)
M(1)-M(2)-O(11)	128.9(2)	127.95(28)	125.4(2)	124.97(27)
M(1)-M(2)-O(12)	123.2(3)	123.01(27)	127.9(2)	127.5(3)

M(3)-M(2)-O(4)	52.1(2)	51.98(24)	52.1(2)	52.79(25)
M(3)-M(2)-O(5)	54.0(2)	54.26(23)	53.6(2)	53.71(24)
M(3)-M(2)-O(6)	52.0(2)	52.23(27)	52.0(2)	52.19(25)
M(3)-M(2)-O(7)	110.5(2)	110.98(25)	111.0(2)	111.27(26)
M(3)-M(2)-O(11)	126.9(3)	125.4(3)	126.9(2)	126.48(28)
M(3)-M(2)-O(12)	126.9(3)	126.20(28)	123.2(2)	123.68(27)
O(4)-M(2)-O(5)	92.3(3)	92.9(3)	91.8(3)	92.6(3)
O(4)-M(2)-O(6)	86.5(3)	86.4(4)	85.2(3)	85.5(4)
O(4)-M(2)-O(7)	86.5(3)	87.5(4)	83.1(3)	83.9(4)
O(4)-M(2)-O(11)	178.5(3)	177.2(4)	177.3(3)	177.7(4)
O(4)-M(2)-O(12)	86.7(3)	86.0(4)	87.4(3)	86.5(4)
O(5)-M(2)-O(6)	82.0(3)	81.9(4)	83.5(3)	83.8(3)
O(5)-M(2)-O(7)	80.5(3)	80.9(3)	84.7(3)	84.0(4)
O(5)-M(2)-O(11)	87.7(3)	85.7(4)	85.9(3)	85.5(4)
O(5)-M(2)-O(12)	177.0(3)	177.5(4)	175.8(3)	176.8(4)
O(6)-M(2)-O(7)	160.9(3)	161.4(4)	163.0(3)	163.4(4)
O(6)-M(2)-O(11)	92.0(3)	91.0(4)	95.9(3)	95.6(4)
O(6)-M(2)-O(12)	100.7(3)	100.3(4)	92.3(3)	93.1(4)
O(7)-M(2)-O(11)	94.9(3)	94.6(4)	95.4(3)	94.6(4)
O(7)-M(2)-O(12)	96.7(3)	96.9(4)	99.3(3)	98.9(4)
O(11)-M(2)-O(12)	93.4(3)	95.4(4)	95.0(3)	95.5(4)
M(1)-M(3)-M(2)	60.0(0)	59.83(3)	60.2(0)	60.16(27)
M(1)-M(3)-M(4)	52.1(2)	52.55(24)	52.0(2)	52.77(25)
M(1)-M(3)-M(5)	54.4(2)	54.65(24)	54.2(2)	54.03(24)
M(1)-M(3)-M(6)	110.9(2)	110.36(27)	111.4(2)	111.13(24)
M(1)-M(3)-M(8)	51.7(2)	52.04(27)	52.3(2)	52.35(25)
M(1)-M(3)-M(9)	125.9(2)	125.5(3)	127.6(2)	126.62(28)
M(1)-M(3)-M(13)	127.3(3)	126.8(3)	12o.3(2)	125.75(28)
M(2)-M(3)-O(4)	52.0(2)	52.61(22)	52.1(2)	52.30(25)
M(2)-M(3)-O(5)	54.3(2)	54.07(23)	54.3(2)	54.96(24)
M(2)-M(3)-O(6)	51.0(2)	50.64(27)	51.2(2)	50.99(24)
M(2)-M(3)-O(8)	111.7(2)	111.86(27)	112.4(2)	112.41(25)
M(2)-M(3)-O(9)	128.6(2)	127.81(27)	128.0(2)	127.2(3)
M(2)-M(3)-O(13)	124.7(3)	124.3(3)	125.9(2)	125.7(3)
O(4)-M(3)-O(5)	92.4(3)	93.2(3)	92.3(2)	93.2(3)
O(4)-M(3)-O(6)	85.7(3)	85.7(4)	84.6(3)	84.3(3)
)(4)-M(3)-O(8)	84.4(3)	84.7(4)	86.4(3)	87.2(4)
)(4)-M(3)-O(9)	177.7(3)	177.9(4)	179.6(3)	179.3(4)
O(4)-M(3)-O(13)	88.0(3)	86.6(4)	88.2(3)	87.1(4)
O(5)-M(3)-O(6)	81.5(3)	80.7(4)	83.4(3)	83.8(3)
O(5)-M(3)-O(8)	84.2(3)	84.7(4)	82.8(3)	81.9(3)
O(5)-M(3)-O(9)	86.7(3)	85.8(3)	87.5(3)	86.1(4)
O(5)-M(3)-O(13)	177.7(4)	177.5(4)	179.5(3)	179.3(4)

O(6)-M(3)-O(8)	162.2(3)	162.9(4)	163.2(3)	162.9(3)
O(6)-M(3)-O(9)	96.2(3)	96.0(4)	95.7(3)	95.7(4)
O(6)-M(3)-O(13)	96.3(4)	96.8(4)	96.3(3)	96.9(4)
O(8)-M(3)-O(9)	93.4(3)	93.3(4)	93.2(3)	92.6(4)
O(8)-M(3)-O(13)	98.1(3)	97.8(4)	97.6(3)	97.5(4)
O(9)-M(3)-O(13)	92.9(3)	94.4(4)	92.0(3)	93.6(4)
M(1)-O(4)-M(2)	75.9(3)	74.82(28)	76.1(3)	75.1(3)
M(1)-O(4)-M(3)	75.7(3)	75.3(3)	75.8(3)	74.5(3)
M(2)-O(4)-M(3)	75.8(3)	75.4(3)	75.7(3)	74.9(3)
M(1)-O(5)-M(2)	71.5(1)	71.12(26)	72.0(2)	71.51(27)
M(1)-O(5)-M(3)	71.5(2)	71.13(26)	72.1(2)	71.9(3)
M(2)-O(6)-M(2)	77.1(3)	77.1(3)	76.8(3)	76.8(3)
M(1)-O(7)-M(2)	77.4(3)	76.8(3)	77.2(3)	77.0(3)
M(1)-O(8)-M(3)	77.6(3)	76.9(3)	76.8(3)	76.8(3)

Table IV. Electrochemical Data[a]

$M_3O(OPr^i)_{10}$	$E_{1/2}$(red),V	$E_{1/2}$,mV	Ep(ox),V
Mo_3	-1.46	110	0.48
Mo_2W	-1.57	175	0.20
W_3	-2.16	140	0.09

[a]THF solution, 0.01 F $AgNO_3(CH_3CN)$/Ag ref. electrode. See experimental section.

Table V. UV-Visible Absorption Spectra, Hexane Solution

$M_3O(OPr^i)_{10}$	γ_{max}, nm (ϵ, $LM^{-1}cm^{-1}$)
Mo_3	690(330), 430(560), 287(25,000), 240(18,000)
Mo_2W	718(515), 420sh(~650), 270(30,000)
W_3	600(565), 420sh(~260), 350sh(~1600), 248(30,000)

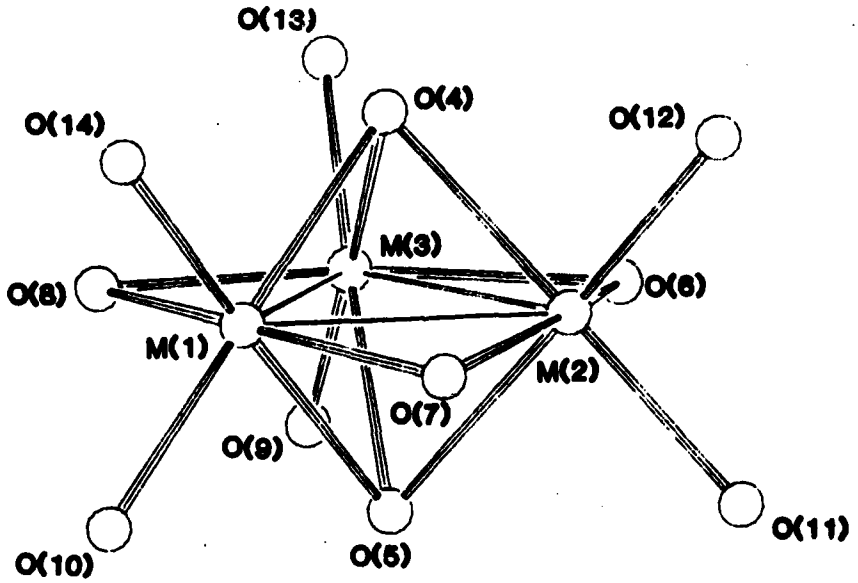
Table 6: Crystal Data Summary

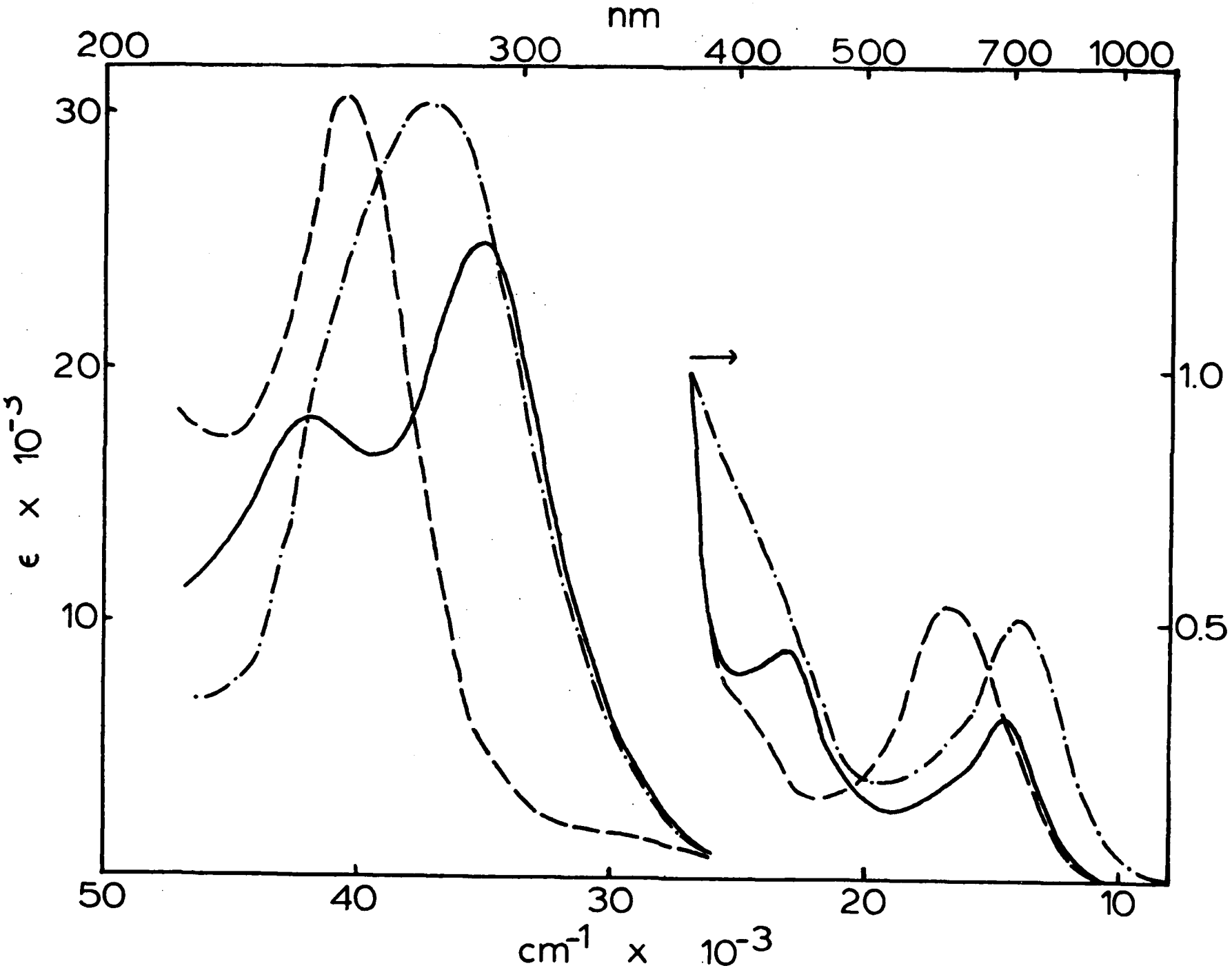
Empirical Formula	$W_3O_{11}C_{30}H_{70}$
Color of Crystal	Black
Crystal Dimensions (mm)	.08 x .07 x .04 mm
Space Group	$P\bar{1}$
Cell Dimensions	
Temperature (°C)	-160
a (Å)	21.303(5)
b (Å)	21.809(6)
c (Å)	10.265(2)
alpha (deg)	98.74(1)
beta (deg)	92.93(1)
gamma (deg)	117.93(1)
Z (Molecules/cell)	4
Volume ($Å^3$)	4123.87
Calculated Density (gm/cm^3)	1.866
Wavelength (Å)	.71069
Molecular Weight	1158.43
Linear Absorption Coefficient (cm^{-1})	85.749
Detector to sample distance (cm)	22.5
Sample to source distance (cm)	23.5
Average omega scan width at half height	.25
Scan speed (deg/min)	4.0
Scan width (deg + dispersion)	2.0
Individual background (sec)	6
Aperture size (mm)	3.0 x 4.0
Two-Theta Range (deg)	6 - 45
Total number of reflections collected	10986
Number of unique intensities	0
Number of F > 2.33 sigma(F)	0
R(F)	.0467
Rw(F)	.0487
Goodness of Fit for the last cycle	1.404
Maximum delta/sigma for last cycle	.05

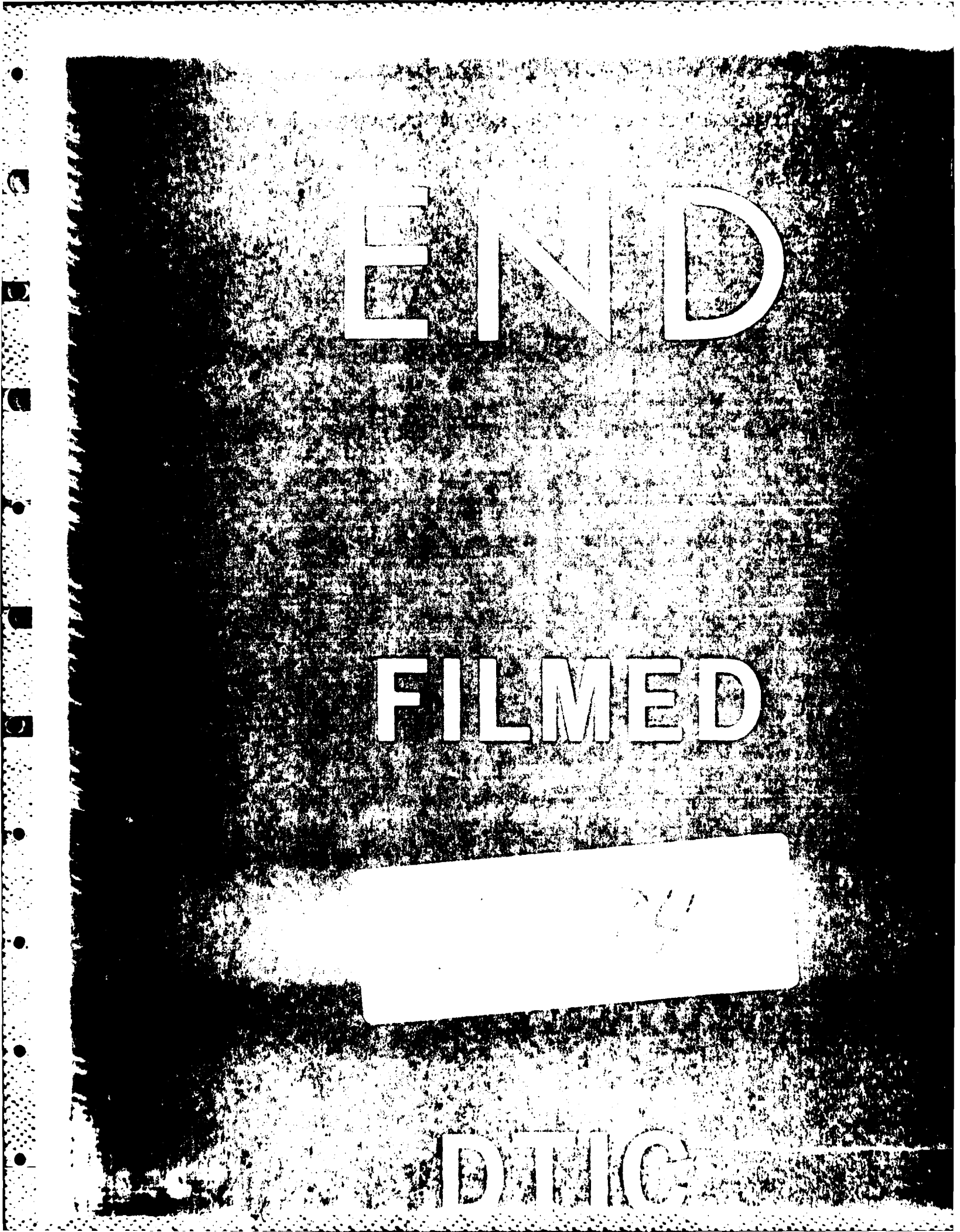
CAPTIONS TO FIGURES

Figure 1. The central M_3O_{11} skeleton of the $W_3O(O\text{-}i\text{-}Pr)_{10}$ molecule showing the number scheme for the metal and oxygen atoms. This is the same number scheme used previously for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ molecule. O(4) is the capping oxo group.

Figure 2. A comparison of the electronic absorption spectra, recorded in hexane, for the oxo capped triangulo metal isopropoxides, where ——— represents $Mo_3O(O\text{-}i\text{-}Pr)_{10}$, — — — $W_3O(O\text{-}i\text{-}Pr)_{10}$ and — · — · $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$.


O(13)
O(4)
O(14)
O(12)
M(3)
O(8)
O(6)
M(1)
M(2)
O(7)
O(9)
O(10)
O(5)
O(11)


nm
200
300
400
500
700
1000
30
20
10
ε x 10⁻³
1.0
0.5
50
40
30
20
10
cm⁻¹ x 10⁻³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